

Exclusive production of excited-state sulfur (^1D) atoms from 193 nm photolysis of thietane

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Abstract

Tunable synchrotron radiation has been used to probe the dissociation dynamics of thietane ($\text{C}_3\text{H}_6\text{S}$) at 193 nm, providing selective determination of the translational energy distribution of both excited (^1D) and ground-state (^3P) sulfur atoms, with momentum-matching to the C_3H_6 co-fragment. The results suggest that the sulfur atom is produced almost exclusively in its excited (^1D) state, with ground-state (^3P) production less than 5%. The first single-photon ionization efficiency (PIE) spectrum for the $\text{S}(^1\text{D})$ state with a resolution of 0.2 eV is reported. © 2002 Elsevier Science B.V. All rights reserved.

Spin conservation is rarely expected in chemical reactions of large molecular systems and is only occasionally observed in small molecules. This is particularly the case for the dissociation of large molecules in which potential energy surfaces are often strongly coupled. It is thus of considerable surprise to find that the loss of a sulfur atom from thietane, (*c*- $\text{C}_3\text{H}_6\text{S}$) a four-membered ring compound, generates exclusively the spin allowed, but excited state of the sulfur atom, (^1D). There have

been many photodissociation studies of sulfide compounds (Table 1). In all the systems indicated, the parent compounds are in their singlet states as are the product molecules, and thus the corresponding sulfur atom should also be in the singlet (^1D) state. However this is not the case. Presumably the heavy sulfur atom increases the likelihood of intersystem crossing (ISC), and the result is mixed spin sulfur products as can be seen from Table 1. The triatomic OCS system is nearly spin conserved, with 5% going into the triplet channel, while the five-membered ring thiophene produces exclusively ground-state sulfur atoms, even though there is enough energy to generate spin allowed $\text{S}(^1\text{D})$.

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Table 1
The branching ratio of S(³P):S(¹D) from various sulfides

Species	S(³ P)/S(¹ D)	Wavelength (nm)
H ₂ S	0.87/0.13 [1]	193
CS ₂	0.74/0.26 [2]	193
	0.71/0.29 [3]	193
	0.75/0.25 [4]	193
OCS	0.05/0.95 [5]	222
CH ₃ S	0.15/0.85 [6]	193
C ₂ H ₄ S (ethylene sulfide)	0.59/0.41 [7]	193
C ₃ H ₆ S (propylene sulfide)	0.28/0.72 [8]	193
C ₄ H ₄ S (thiophene)	1.0/0.0 [9]	193

The results in Table 1 give some indication of the difficulty in producing pure excited-state sulfur atoms for use in subsequent chemical reactions. While the photoabsorption and photoionization of ground-state sulfur atoms S(³P) have been the subject of numerous theoretical and experimental investigations [10–17], few studies have focused on the first excited state, (¹D), of the sulfur atom [18].

Previous photolysis studies in which thietane was excited at 313 and 254 nm have been carried out by several groups in low pressure reaction cells using gas chromatography product analysis. The only dissociation products detected were C₂H₄ + CH₂S, and no evidence for S atom production was noted even though there is sufficient energy to produce C₃H₆ + S, the latter in both ground or excited states [19–21]. At these photolysis energies, the initial step appears to be the breaking of the C–S bond and the formation of a diradical followed by rearrangement to form ethylene and thioformaldehyde. However, as the excitation energy is increased to 214 nm, the production of C₃H₆ becomes important [22,23]. On the basis of an RRKM theory analysis of the ratio of collisionally stabilized cyclopropane to ring opened propene products as a function of the inert gas pressure, Dorer et al. [22] concluded that the sulfur atom is formed predominantly in the ³P ground state.

We report here the use of tunable (6–20 eV) synchrotron undulator radiation, to probe the sulfur and C₃H₆ products, as well as the molecular channels of the photodissociation of thietane at

193 nm. These experiments permit not only the determination of the product translational energy in a collisionless environment, but also their internal energy. The experiments were performed at the Chemical Dynamics beamline 9.0.2 of the Advanced Light Source using a rotating source molecular beam apparatus described in detail elsewhere [24,25]. A 7.5% thietane sample in 700 Torr of He, introduced as a pulsed and skimmed molecular beam, was photolyzed by a 193 nm ArF excimer laser. The small fraction of the dissociation products that scatters toward the detection region 15.2 cm from the photolysis point, were photoionized using synchrotron undulator radiation. Time-of-flight (TOF) spectra of neutral photofragments were measured at several scattering angles for the following ions: CH₂S⁺, C₃H₆⁺, C₃H₅⁺, C₃H₄⁺, H₂S⁺, HS⁺, S⁺, and C₂H₄⁺. In this communication, we describe only the results for the S + C₃H₆ reaction, which is a major channel for the dissociation at this photolysis wavelength. We estimate that the S(¹D) + C₃H₆ channel represents about 60% of the total dissociation paths. This branching ratio is difficult to determine quantitatively because of the unknown photoionization cross section for the free radicals associated with the other major product channel, HS + C₃H₅.

One of the unique features of detecting products by tunable photoionization is the ability to distinguish products that have different ionization energies. Photolysis at 193 nm permits sulfur atoms to be formed in any of three electronic states, whose ionization energies are: 10.36 eV (³P), 9.21 eV (¹D), and 7.61 eV (¹S). Photon energies between 7.61 and 9.21 eV will ionize only the ¹S state, while energies between 9.21 and 10.36 eV will ionize only the two excited states. Finally, above 10.36 eV, all three states can be ionized. We have successfully applied this method to selectively probe S(³P) and S(¹D) from photodissociation of CS₂ [4], ethylene sulfide [7] and propylene sulfide [8].

Fig. 1a shows a TOF spectrum of the $m/e = 32$ (S⁺), signal from the photoionization of sulfur atoms, at a scattering angle of 15°. The photon energy for this spectrum was 9.6 eV, which is below the IE of the ground-state S(³P). Hence, only excited-state S(¹D) and/or S(¹S) species contribute to the data in

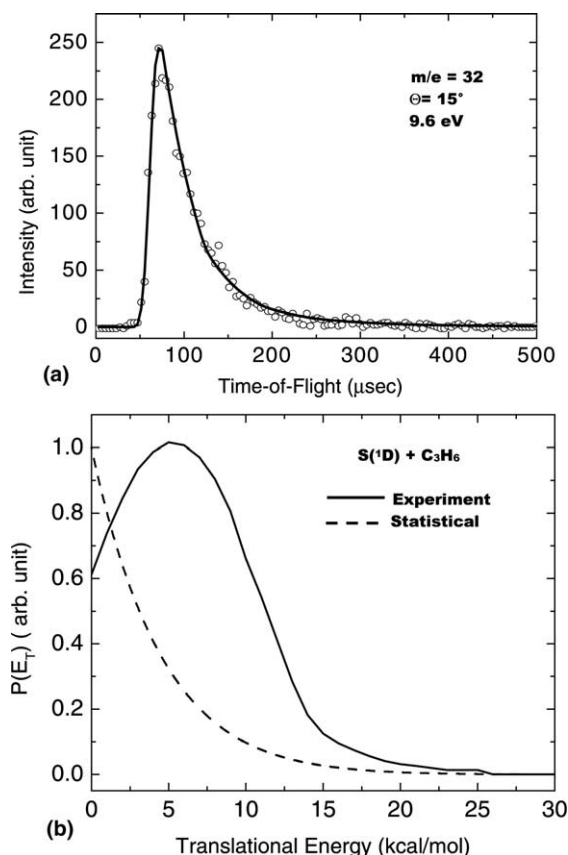


Fig. 1. (a) TOF spectrum of the S atom ($m/e = 32$) at a scattering angle of 15° . The photon energy used to ionize the products was 9.6 eV. The open circles are experimental data, while the solid line is the calculated TOF distribution using the total translational energy distribution, $P(E_T)$, for the $S + C_3H_6$ reaction as shown in (b). The dashed line in (b) shows the statistically expected translational energy distribution.

Fig. 1. However, as will be shown, the latter does not contribute. The translational energy distribution shown in Fig. 1b was used to fit the data by forward convolution with the instrumental function. The translational energy peaks at approximately 5 kcal/mol, extends to about 30 kcal/mol, and has an average energy of 6.8 kcal/mol. The C_3H_6 fragment TOF distribution (not shown here) was measured as well, and its distribution was fit with the same $P(E_T)$ distribution shown in Fig. 1b. Because the two fragments have the same momentum (in opposite directions), the same $P(E_T)$ distribution must fit the two sets of data.

Fig. 2 shows the normalized TOF spectra of S^+ at a scattering angle of 15° at photon energies of 9.6, 10.0, and 10.7 eV. These three distributions are identical. If more than one electronic state had contributed to the signals, the TOF distributions should have changed with photon energy. Forward convolution analysis of the TOF spectra indicate the ground-state sulfur contribution is less than 5% of the total TOF signal. Because no signal is produced below 9.3 eV, where $S(^1S)$ atoms would ionize, these results indicate that the sulfur atom is produced exclusively in the excited 1D state. This is entirely different from the S atoms produced from photolysis of other organo-sulfur compounds, as well as the simplest sulfides such as H_2S [1] and CS_2 [4], which all produce mixtures of ground- and excited-state sulfur atoms that are easily distinguished by their different TOF distributions.

Because the C_3H_6 product is a singlet, spin conservation demands that the sulfur be produced in the singlet state. However, previously mentioned studies at lower photolysis energies indicate that excited thietane breaks up by the initial formation of the diradical, $\cdot CH_2CH_2CH_2S\cdot$, which at lower energies has sufficient time to fragment to ethylene and CH_2S . Under these circumstances it would seem that intersystem crossing to the triplet surface should be possible. Because we see no evidence of $S(^3P)$ production, the production of S atoms at 193 nm must involve a concerted release

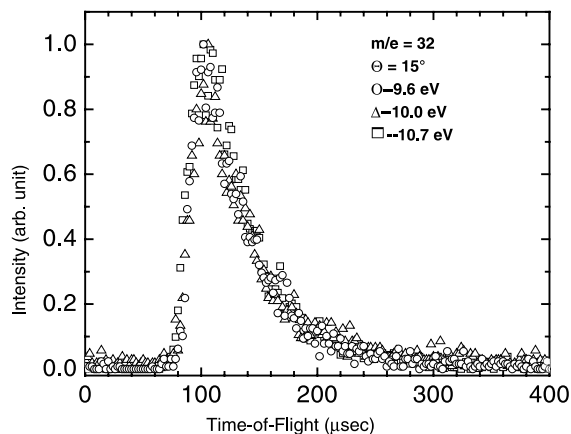


Fig. 2. TOF spectra of S ($m/e = 32$) at the three indicated probe photon energies and the scattering angle of 15° .

of the S atom and a simultaneous formation of the three-membered hydrocarbon ring. It thus remains on the singlet surface. If a diradical were formed, the lower energy ethylene plus CH_2S reaction channel would dominate. In fact, just the opposite is observed with the S release being the dominant dissociation channel.

A concerted mechanism is also supported by the translational energy distribution shown in Fig. 1b. The 193 nm (148.1 kcal/mol) photolysis of thietane with the production of the excited S^1D and cyclopropane leaves an available energy (E_{avl}) of 56.9 kcal/mol for distribution among the translational, rotational, and vibrational degrees of freedom. This assumes the following 298 K heats of formation in kcal/mol: thietane (14.5) [26], cyclopropane (12.7) [26]. The S^1D energy of 93.2 kcal/mol is determined by adding the ground-state heat of formation of 66.6 kcal/mol [27] to the excited-state energy of 9239 cm^{-1} (26.4 kcal/mol) [28]. The dashed line in Fig. 1b shows the statistically expected translational energy distribution, which is calculated by incorporating conservation of angular and linear momentum in a global manner [29]. A two-dimensional phase space theory translational energy distribution is combined with a ro-vibrational density of states for the product cyclopropane (vibrational frequencies obtained from [30]), so that the translational energy distribution is given by

$$P(E_{\text{t}}) \propto \rho_{\text{r,v}}(E_{\text{avl}} - E_{\text{T}}).$$

As is evident, the experimental distribution is quite different from the statistically expected one in both the average energy 6.8 kcal/mol vs 4.1 kcal/mol, and in the general shape. This indicates that the products are being produced along a specific potential energy surface where equilibration of the various energy modes is incomplete.

The ability to produce a pure excited state of the S atom, makes the 193 nm photodissociation of thietane a potentially very important method for producing such atoms for spectroscopic or dynamical studies. The first single-photo ionization efficiency (PIE) spectrum of the S^1D , obtained by scanning the undulator with its resolution of about 0.2 eV, is shown in Fig. 3. The onset at about 9.2 eV is close to the IP of S^1D .

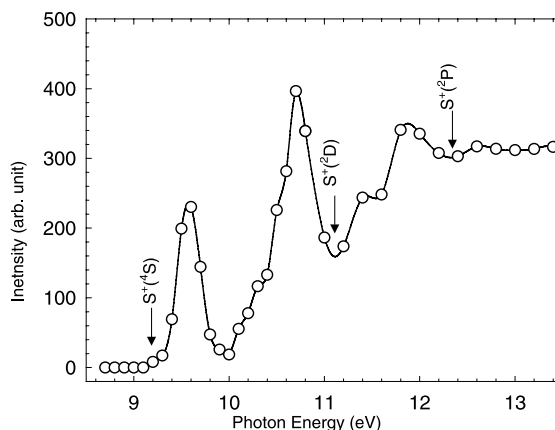


Fig. 3. Photoionization efficiency curve of S^1D from 193 nm photodissociation of thietane at the scattering angle of 15° . Arrows indicate the transitions from S^1D to $\text{S}^+(^4\text{S})$, $\text{S}^+(^2\text{D})$, and $\text{S}^+(^2\text{P})$, respectively.

Three obvious peaks at 9.6, 10.7, and 11.9 eV, are due to autoionizing Rydberg states that are only partially resolved in our spectrum. They approximately coincide with previously measured [13,15] states if one shifts the spectrum to lower energies by the energy difference of 1.15 eV between the S^1D and S^3P states. Such a shift is expected since the Rydberg states converge to the same final ion states, $\text{S}^+(^2\text{D}^0)$ at 11.05 eV, and $\text{S}^+(^2\text{P}^0)$ at 12.25 eV. These limits are indicated in the Figure. However, because of the single starting state, only singlet excited states will be produced with significant intensities. Plans are presently underway to measure a high resolution photoionization efficiency spectrum of the S^1D state using a 6.65 m monochromator that will yield a resolution of 0.5 meV. Such a study will be complementary to both the one photon spectrum of S^3P of Gibson et al. [13] and the two-photon experiment on S^1D reported by Pratt [18].

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